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(19) (CA) # CANADIAN PATENT

(54) OIL DISPERSING COMPOSITION AND ITS USE

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Background of the Invention

Oil in a form and quantity sufficient to be visibly apparent is nearly always objectionable even though the amount is not great. For example, oil found in industrial receiving streams is generally not present in great concentrations but is present in an amount which is visible as floating oil. Because of leaks in cooling water systems of refineries, discharge of waste waters from foundries, steel production facilities and smelting operations where oil is used for one purpose or another, small concentrations of oil are discharged to the receiving streams.

Although the amount of oil discharged is not a significant amount, the discharge becomes objectionable since it appears as floating oil on the surface of the water of the stream. This floating oil is objectionable not only aesthetically, but also from an operational and use standpoint. For example, water to be used for potable purposes must be specially treated in order to remove even minute quantities of oil; otherwise, the taste will be somewhat objectionable. Problems caused by floating oil in the environment and on wildlife per se are obvious and have been well-documented and, accordingly, need not be expounded upon.

Various metals have found widespread use as dispersants, weighting agents and adsorbents in an effort to solve the problem of floating oils. The oil films which are of very small thicknesses are visible because of the bright bands of color which are apparent. Although quite thin, these films do cause significant problems when they collect on the bodies of foul and fish, on waterside structures and on the beaches and shores of receiving streams. It was the present inventors' feeling that if this floating oil could be dispersed in small droplet form, the oil could be more readily attacked by the bacteria contained in a receiving stream, ponds, or lagoon because of the increase in surface area of the oil. Since the bacteria could more rapidly consume the droplets of oil, the amount of oil which remains to collect could be minimized.

It was the present inventors' contention that the oily films which occur on the surface of water were strictly due to the high interfacial tensions eoncountered between the oil and the water. As is well-known, it is extremely difficult to mix oil and water and maintain a stable suspension of the oil droplets in the water. Accordingly, the inventors' objective was to produce a composition which would decrease the interfacial tension between the oil film and disperse the oil in the water. If the oil could be dispersed effectively, the oil droplets, because they are now completely surrounded by the water, would be more vehemently attacked by the bacteria contained in the water. Not only then would the problem of floating oil be resolved, but also effluent standards could be observed. There are presently many federal and state restrictions on the oil content of the effluent water. In this regard, it should be mentioned that the first restriction is based upon total oil, i. e. the oil contained not only on the surface of the water, but also contained in the water itself. The second restriction is to floating oil. The second restriction is much more severe because there is no allowable limit, i. e. there is to be no floating oil. Many facilities successfully live up to the standards with respect to total oil but have not been able to successfully cope with the prohibition relative to floating oil.

General Description of the Invention

The present inventors found that if a compound prepared in accordance with the following procedure and with the respective ingredients set forth were added to an aqueous medium containing oil, that the oil would successfully disperse in the medium because of the materials or product's capability of decreasing the interfacial tension between the oil and the water. The final product which is used in accordance with the invention is prepared by reacting at least one aliphatic carboxylic acid having from 10 to 20 carbon atoms with at least one compound having a 1, 2 ethylenediamine moiety. The mole ratios of the respective reactants appear to be somewhat

critical in order to insure that the resulting product possesses the desired capacity to reduce the surface tension between the oil and the water. The mole ratio of the carboxylic acid to the diamine compound should be from about 0.5:1 to about 1.5:1. The reaction is carried out in two stages: the first being at a temperature and for a time sufficient to produce an amidification product. This reaction temperature is quite high since at lower temperatures, reactions between the two reactants will produce a salt which will not effectively operate in the second reaction which is required to produce the instant product.

After the amidification stage, the resulting product is heated at a temperature and for a time sufficient to produce a final product. It is believed that the reactants reacted in the manner described above produce a mixture of products which is composed primarily of imidazolines which in the primary instance are amine terminated and in some cases amid terminated. The structures of the compounds believed to be primarily formed will be discussed later in this application.

Preferably the mole ratio of the carboxylic acid to the diamine compound is from about 0.8:1 to about 1:1 with the amidification temperature being from about 230 to about 330°F with the reaction time from about 3 to about 7 hours. The cyclization temperature preferably is from about 350°F to about 450°F with a time of from about 4 to about 10 hours.

The most successful products have been prepared from carboxylic acids having from 12 to 18 carbon atoms and more so from a mixture of carboxylic acids each having from about 12 to 18 carbon atoms. The specific carboxylic acids which have been most successfully used are contained in a material generally referred to as refined tall oil fatty acids. Refined tall oil fatty acids generally contain a mixture of unsaturated carboxylic acids. These successful products are based on a reaction between the aforementioned carboxylic acids and diethylene triamine under the conditions prescribed herein. In addition to the predominantly formed amine terminated product

along with some amide terminated product as described infra, an ambiguous mixture of uncyclized amides (practically impossible to isolate) also form. For this reason, it is extremely difficult to ascertain the respective ingredients which have major responsibility for the effectiveness of this material.

The diamines which have been successful for the purpose may be exemplified, but certainly not limited to anyone of the following: ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine, pentaethylenehexamine, etc. and the obvious homologues substituted derivatives thereof.

It was found that when the final product as produced in accordance with the above was added to an aqueous medium containing floating oil, for example in the amount of 0.5 to 1,000 parts per million, that the interfacial tension between the water and oil was significanly reduced to the extent that the oil film became suspended in the water. Preferably, and in most instances, a treatment of from about 1 to 200 parts per million will be satisfactory for the purpose.

The efficacy of the final product to perform as desired can be ascertained by measuring interfacial tension between the water and oil as it naturally occurs and then measuring such after the final product has been added. In addition, and for most practical purposes, a simpler test and quite effective test particularly with respect to floating oil is commonly used, that is the visual test. As earlier stated, oil films of microscopic thicknesses give rise to bright bands of color which are so often observed on the surface of water. If in fact a dispersant is successful in destroying the surface film of oil, then the bright bands of color would no longer be apparent.

A particularly successful composition containing the final product of the invention has been produced by mixing or dissolving the final product in an alcohol. Preferably, the alcohol should contain from

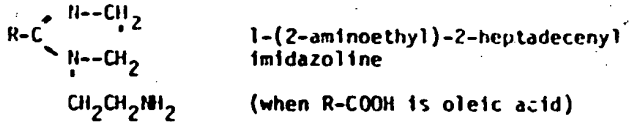
1 to 10 carbon atoms either in a linear or branched chain. Examples include methanol, ethanol, propanol, hexanol, decanol and branched alcohols such as isopropanol, isohexanol, 2-ethyl hexanol, etc.

The composition may contain from 5 to 95% by weight of the final product and, conversely, from 95 to 5% by weight of the alcohol. Compositions containing from about 60 to 90% of the alcohol and, conversely, from 10 to 40% of the final product have been found to be particularly effective.

As earlier stated, the products formed are believed to be for the most part derivatives of imidazoline and the mode of preparation of these compounds is felt to be explained by the reaction equation which follows:

$$R\text{-}COOH + H_2N\text{--}CH_2CH_2\text{--}NH\text{--}CH_2CH_2NH_2 \xrightarrow[\text{Temperature}]{\text{Amidification}}$$

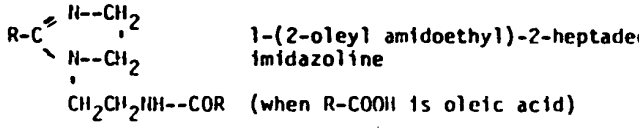
$$R\text{-}\overset{\overset{OH}{|}}{C}N\text{--}CH_2\text{--}CH_2NH\text{--}CH_2CH_2NH_2 + H_2O\uparrow \xrightarrow[\text{Temperature}]{\text{Cyclization}}$$



1-(2-aminoethyl)-2-heptadecenyl imidazoline (when R-COOH is oleic acid)

Amine terminate imidazoline

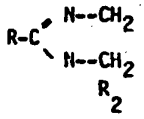
In most instances a portion of the amine terminated imidazoline amidifies to form the amide terminate imidazoline having the structural formula



1-(2-oleyl amidoethyl)-2-heptadecenyl imidazoline (when R-COOH is oleic acid)

Because of the various reaction conditions and the various products formed, it is difficult to ascertain the exact ingredients of the final product, and more so, with respect to the concentration of each.

The ingredient which is thought to be the active ingredient in the sense of the present invention appears to be the final product having the formula



where R is the residue of the fatty aliphatic acid used and having from 9 to 19 carbon atoms; and R_2 is the residue of the 1, 2 di-amino compound used to prepare the product, for example, R_2 might represent--CH_2CH_2 NH--CH_2CH_2NH--$CH_2CH_2NH_2$ when the reactant was tetraethylene pentaamine, etc.

SPECIFIC EMBODIMENTS:

Example 1

The reactants used to produce the final product of the invention were as follows:

1. A refined tall oil fatty acid having the following composition:

   50% oleic acid
   31.2% conjugated linoleic acid
   13.3% saturated acids (e. g., palmitic, stearic, arachidic, behenic)
   2.8% conjugated linolenic acid
   2.7% conjugated palmitolenic acid

2. A polyalkylene polyamine having the formula:

   NH_2-CH_2CH_2-NH-CH_2CH_2-NH_2 (diethylene triamine)

A 2,000 gallon reactor condenser was charged with 8,720 pounds of the refined tall oil fatty acid described above. The refined tall oil fatty acid in the condenser reactor was agitated for a period of 30 minutes after which 3,860 pounds of diethylene triamine were added thereto. The mixture in the reactor was agitated for a period of 30 minutes and then 850 pounds toluene were added. The mixture of the refined tall oil fatty acids, the ethylene diamine and the toluene was then heated at 250°F for a period of 4 hours after which the distillate was drained from the reaction medium. After removal of the distillate, the batch was then heated to a temperature of 390°F for 6-1/2 hours. The reaction medium was then allowed to cool.

The final product produced in this manner contained primarily the imidazoline which has been described supra when the R-COOH of the reaction equation represented oleic acid. Because of the predominance of the oleic acid in the refined tall oil fatty acids, it is predicted that the primary ingredient formed was a derivative of that acid.

Example 2

The product as prepared as described in Example 1 was mixed with a quantity of 2-ethyl hexanol. The relative proportions of the ingredients of the composition were determined on a weight basis. The resulting alcoholic solution contained approximately 85% by weight of alcohol and 15% by weight of the product produced in accordance with Example 1.

Example 3

A composition was prepared in the method described for Example 2 above with the exception that the alcohol utilized was isopropanol. The quantity of the alcohol and the final product in the composition remained the same.

Example 4

A composition was prepared in the method described for Example 2 above with the exception that the alcohol utilized was 2-ethyl butanol. The quantity of the alcohol and the final product in the composition remained the same.

Example 5

A composition was prepared in the method described for Example 2 above with the exception that the alcohol was isodecanol. The quantity of the alcohol and the final product in the composition remained the same.

In order to establish the capacity of the final product of the invention to reduce the interfacial tension between water and oil, various oil-in-water mixtures were produced and the interfacial tensions measured before and after addition of various alcohols as set forth in Examples 3 through 5.

The interfacial tensions were measured according to standard practices using a Du Nouy tensiometer (ASTM D971-50).

TABLE 1

Material Used: Final product of Example 1
ppm = parts per million parts of oil-water medium

Type Oil	Interfacial Tensions (dynes/cm) at feed rates of the final product				
	0 ppm	5 ppm	10 ppm	20 ppm	50 ppm
No. 1 heating oil (mixed hydrocarbons)	22.9	19.4	14.5	5.5	----
Vegetable oil (cottonseed and olive oil mix)	16.9	14.7	14.9	13.4	9.1
Light aromatic fraction (i. e., benzene, toluene, xylene)	29.0	23.0	21.5	20.4	19.3

Light naphtha (low boiling mixed hydrocarbons-- boiling range 240°-340°F)	33.8	18.0	14.7	11.4	4.2
Heavy aromatic naphtha (aromatic hydrocarbons boiling range 350°-550°F)	28.0	20.0	20.7	16.0	16.4

From the data above, it is apparent that the final product of Example 1 was quite effective in reducing the interfacial tension in all cases.

The following data relative to interfacial tension was recorded when the composition of Example 2 was added to the various oil-water phase. This composition contained only 20% by weight of the final product and 80% by weight of the 2-ethyl hexanol.

TABLE 2

Type Oil	Interfacial Tensions (dynes/cm)				
	0 ppm	5 ppm	10 ppm	20 ppm	50 ppm
No. 1 heating oil	22.9	19.4	15.8	10.5	3.8
Light aromatic fraction	29.0	27.5	20.0	16.0	15.0
Light Naphtha	33.8	19.7	13.3	8.5	4.4
Heavy aromatic naphtha	28.0	21.8	22.0	20.0	17.8

The composition of Example 2 was quite effective for the purpose considering that it contained only 20% by weight of the final product of Example 1.

In order to ascertain the operability and utility of compositions containing the final product of Example 1 with other acids, the compositions of Examples 3, 4 and 5 were tested at various treatment ranges utilizing the Light Aromatic Fraction and the Heavy Aromatic Naphtha oils as representative of the oils. The interfacial tensions measured are recorded in Table 3.

TABLE 3

Type Oil	Composition of	Interfacial Tension				
		0 ppm	5 ppm	10 ppm	20 ppm	50 ppm
Light aromatic fraction	Ex. 3	29.0	26.8	23.9	21.8	19.3
" " "	Ex. 4	29.0	24.9	24.8	23.0	20.0
" " "	Ex. 5	29.0	24.9	24.7	23.1	20.3
Heavy aromatic naphtha	Ex. 3	28.0	19.3	17.9	13.3	16.2
" " "	Ex. 4	28.0	23.0	21.7	17.0	16.1
" " "	Ex. 5	28.0	23.9	22.4	18.5	17.1

The data obtained and recorded in Table 3 clearly established that the composition was effective for the purpose.

Example 6

To establish the efficacy of the inventive composition on a practical basis, a steel mill which possessed unacceptable floating oil in its discharge water was chosen for a test. Although well under the acceptable standards set for the total oil contact of effluent, the mill was having a certain amount of difficulty removing the floating oil. In the particular jurisdiction, the discharge of any effluent which contained floating oil was prohibited. As in all instances of floating oil, the floating oil was distinctly apparent by virtue of the very predominant colored bands. A point in the effluent stream where the number of bands of color were predominant was chosen for the area of application of a portion of the product of Example 1 hereof. By calculating the depth, width and length of the stream at this point, the amount of the aqueous medium could be measured and thus the amount of product could be defined. The amount of product (Example 1) added was approximately 25 ppm. After addition, the effluent immediately downstream of application point was observed carefully. The effectiveness of the product was conclusively discerned since the colored bands were no longer apparent and accordingly no longer existent.

In view of the foregoing then, it was concluded that the product of the invention was quite effective for the purpose of dispersing floating oil.

Having thus described the invention, what we claim is:

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for dispersing oil in an aqueous medium which comprises adding to said medium an amount of about 0.5 to 1000 parts per million of said medium of a final product obtained by:

a. reacting at least one aliphatic carboxylic acid having from 10 to 20 carbon atoms, with at least one compound having a 1, 2-ethylenediamine moiety, the mole ratio of the carboxylic acid to diamine compound being from about 0.5:1 to about 1.5:1, said reaction being conducted at a temperature from about 230 to about 330°F for a time from about 3 to about 7 hours to produce an amidification product; and

b. heating said amidification product to a cyclization temperature from about 350 to 450°F for a time from about 4 to about 10 hours to produce said final product.

2. A process according to claim 1 wherein the mole ratio of the carboxylic acid to the diamine compound is from about 0.8:1 to about 1:1.

3. A process according to claim 1 or 2 wherein the carboxylic acid is a mixture of carboxylic acids each having from about 12 to 18 carbon atoms.

4. A process according to claim 1 or 2 wherein the diamine is selected from the group consisting of ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine and pentaethylene hexamine.

5. A process according to claim 2 wherein said final product is added to said medium in an amount of from about 1 to about 200 parts per million.

6. A process according to claim 5 wherein the carboxylic acid is a refined tall oil fatty acid and the diamine compound is diethylene triamine.

7. A process according to claim 2 wherein said final product is mixed with an alcohol and said mixture is added to said medium.

8. A process according to claim 5 wherein the said final product is mixed with an alcohol having from 1 to about 10 carbon atoms and said mixture is added to said medium.

9. A method according to claim 8 wherein the alcohol is selected from the group consisting of isopropanol, 2-ethyl butanol, 2-ethyl hexanol and iso-decanol.

10. A composition for use as a dispersant for oil in aqueous systems which contains from about 5 to about 95% by weight of an alcohol having from 1 to about 10 carbon atoms; and from about 95 to about 5% of a final product obtained by:

a. reacting at least one aliphatic carboxylic acid having from 10 to 20 carbon atoms, with at least one compound having a 1, 2-ethylenediamine moiety, the mole ratio of the carboxylic acid to diamine compound being from about 0.5:1 to about 1.5:1, said reaction being conducted at a temperature from about 230 to about 330°F for a time from about 3 to about 7 hours to produce an amidification product; and

b. heating said amidification product at a cyclization temperature of about 350 to about 450°F for a time from about 4 to about 10 hours to produce said final product.

11. A composition according to claim 10 wherein the mole ratio of the carboxylic acid to the diamine compound is from about 0.8:1 to about 1:1.

12. A composition according to claim 11 wherein the carboxylic acid is a mixture of carboxylic acids each having from about 12 to 18 carbon atoms and wherein the diamine is selected from the group consisting of ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine and pentaethylene hexamine.

13. A composition according to any of claims 10, 11 and 12

wherein said alcohol is selected from the group consisting of isopropanol, 2-ethyl-hexanol, 2-ethyl butanol and iso-decanol.

14. A composition according to claim 12 wherein the carboxylic acid is a refined tall oil fatty acid and the diamine compound is diethylene triamine.

15. A composition according to claim 14 wherein the alcohol is selected from the group consisting of isopropanol, 2-ethyl hexanol, 2-ethyl butanol and iso-decanol.

16. A composition according to claim 15 wherein the alcohol is 2-ethyl hexanol.

17. A composition according to claim 16 wherein the composition contains about 60 to about 90% by weight alcohol and about 10 to about 40% by weight final product.